



Letter to the Editor

Reply to the Letter to the Editor concerning the comments of Dr. F. Meunier to the article Appl. Catal. B: Environ. 136–137 (2013) 225–238, Kalamaras et al., titled “The effect of La³⁺-doping of CeO₂ support on the water–gas shift reaction mechanism and kinetics over Pt/Ce_{1–x}La_xO_{2–δ}”



Keywords:

WGS
SSITKA
H/D exchange
CO₂ readsorption effect

Dear Editor,

This is with a great interest and pleasure that we have read the letter of Dr. Frederic Meunier commenting the interpretation of some of the experimental SSITKA results of our recent article “The effect of La³⁺-doping of CeO₂ support on the water–gas shift reaction mechanism and kinetics over Pt/Ce_{1–x}La_xO_{2–δ}” [1].

The author in his Letter to the Editor has acknowledged the use of an advanced experimental protocol with *in situ* techniques, *operando* SSITKA–Mass Spectrometry–DRIFTS, with the purpose to elucidate essential mechanistic and kinetic aspects of the WGS reaction over Pt supported on Ce_{1–x}La_xO_{2–δ} ($x=0.0, 0.2$ and 1.0) carriers. We would like to express our gratitude for his appreciation in our research work, but also to thank him for giving us the opportunity to present new advanced experiments to the readership of this Journal working in the field of WGS reaction mechanism on supported metal catalysts, and to provide necessary clarifications and answers related to his comments.

1. CO₂ adsorption and stability

The comments offered and which were related to the adsorption and stability behaviour of carbon dioxide on ceria-based metal oxide surfaces [2,3] finds our strong support. In an earlier paper from our group [4], we have performed transient isothermal adsorption/desorption of CO₂ experiments in order to gather information about the reversibility of the step associated with the carbonate-type species formation. This experiment was simply designed to provide further information for the correct interpretation of the red isotopic shift observed during SSITKA–DRIFTS of WGS on Pt/CeO₂ (see Fig. 7a, ref. [4]) for the IR bands related to the formation of carbonate-type adsorbed species. By no means was the obtained quantitative result of this experiment related to the correction of the “C-pool” for CO₂ readsorption. In fact, in a later publication [5] the red isotopic shift was found to be due to the reversible chemisorption of CO₂ on *non active* catalytic sites of the ceria support, since adsorbed carbonates did not react with water for times even larger than that corresponding to the

completion of the SSITKA–Mass spectroscopy experiment, according to the following DRIFTS experiment performed: 3 vol% ¹²CO/10 vol% H₂O/Ar (30 min, s.s.) → 3 vol% ¹²CO/Ar (10 min) → 3 vol% ¹³CO/Ar (10 min) → 10 vol% H₂O/Ar (t) (see also Fig. 7b, ref. [1]).

2. The complexity in measuring CO₂ intraparticle readsorption

The author has raised one of the most important points related to the application of the SSITKA technique in the WGS reaction, that of readsorption of CO₂ gas product, or alternatively, the discrimination among the truly active “carbon-containing” reaction intermediates, which are found in the carbon-path from the CO reactant to the CO₂ gas product, named “C-pool”, and those formed by the *readsorption of CO₂* gas product on *non active* catalytic sites in a *reversible* manner. Irreversible CO₂ chemisorption should not be considered at all as a likelihood of being measured during SSITKA, since ¹²C-carbonate-type species formed under ¹²CO/H₂O can never be replaced by its equivalent ¹³C-carbonate under ¹³CO/H₂O. This means that irreversible CO₂ chemisorption will not contribute to the ¹²CO₂(g) transient response curve recorded and used to estimate the “C-pool” (Fig. 3, ref. [1]). On the other hand, if the carbon-path of the WGS reaction involves a carbonate-like species as the final *active* species before CO₂ product formation, and if this step is considered reversible, then the concentration of this species will be measured during SSITKA, and it should be considered part of the active “C-pool”.

Shannon and Goodwin [6] were among the first who mentioned that the *internal CO₂ readsorption* on non active catalytic sites is difficult to eliminate during the SSITKA experiment. We also point out here that CO₂ readsorption is an intrinsic process that may occur to a large extent inside the pore system of a basic metal oxide support (the case of supported catalysts), where diffusion of CO₂ competes with the non activated CO₂ adsorption step [7]. For this reason, SSITKA can lead to erroneous estimation of the “C-pool” if the concentration of *non active* CO₂ chemisorption sites is significant compared to the concentration of sites that accommodate the true active “C-containing” intermediates of WGS (e.g. CO-s, HCOO-s (formate), COOH-s (carboxyl)). The question then that logically arises is whether a reliable experimental methodology does exist, not based on the ¹³CO–SSITKA, which is able to quantify either the “CO₂ readsorption” effect, or the concentration of the true active “C-containing” reaction intermediates, “C-pool”.

In the discussed publication [1] we have presented an experimental *operando* methodology that uses the “titration of active reaction intermediates” concept, using water, for the first time, in order to estimate the true active “C-pool” formed under steady-state WGS reaction conditions. This “titration of active reaction intermediates” concept was successfully applied towards the CO/H₂ reaction in the past [8–10], where the *active* “C-containing”

reaction intermediates (e.g. CO-s and CH_x-s) were estimated following the switch CO/H₂ (s.s.) → H₂(t) (on line mass spectrometry was used for gas analysis). It was proved that the concentrations of both CH_x-s and CO-s were very similar to those estimated by the ¹³CO-SSITKA experiment. The experiment designed and reported in Fig. 8 of the discussed publication [1] is exactly the application of this “titration of active reaction intermediates” concept. The experiment involved the sequence of the following step gas switches: 3 vol% CO/10 vol% H₂O/Ar (30 min) → 3 vol% ¹²CO/Ar (10 min) → 3 vol% ¹³CO/Ar (10 min) → 10 vol% H₂O/Ar (t). During the CO/H₂O gas switch, active and inactive “C-containing” species were formed. The switch to the ¹²CO/Ar had the purpose to stop the WGS reaction and at the same time to keep the surface coverages of adsorbed CO and those intermediates reversibly interacting with CO(g) the same to those formed under WGS. During this switch, DRIFTS spectra recorded revealed no change in the IR band intensity of adsorbed CO, and only a very small change in the intensities of the IR bands due to formate (HCOO-) species. Upon the switch to the ¹³CO/Ar, it was found that the IR bands of formate species on the support and those due to the adsorbed CO on Pt provided the red isotopic shift. During the last switch to the 10 vol% H₂O/Ar gas mixture, the mass spectrometer was used to record the H₂, ¹²CO₂ and ¹³CO₂ gas production (Fig. 8, ref. [1]), whereas DRIFTS spectra (Fig. 7, ref. [1]) were also recorded (*operando methodology*). The amount of ¹³CO₂ formed was estimated to be 54.7 μmol g⁻¹ (θ=2.1), and that of ¹²CO₂ was 5.4 μmol g⁻¹ (θ=0.2). The obtained DRIFTS results upon the H₂O/Ar gas switch were as follows: (i) all formate bands (2750–3000 cm⁻¹ range) disappear after 5 min on stream, (ii) not all adsorbed CO could be reacted with water (presence of *active* and *inactive* CO-s species) after 5 min on stream, and (iii) the IR bands due to carbonates hardly changed.

The amount of ¹³CO₂ formed (θ=2.1) relates to the titration of the active reaction intermediates, to be associated with adsorbed CO-s and HCOO-s, as clearly identified by SSITKA-DRIFTS. The amount of “C-pool” estimated from the SSITKA experiment (after correcting for the interparticle CO₂ readsorption effect) was θ=2.8 [1]. We argue that the difference in the two amounts of CO₂-s (θ=0.7) represents the amount of “CO₂ readsorption”. On the basis of the above clarifications, the “C-pool” estimated via the SSITKA-Mass spectrometry experiment was overestimated by 33% from the actual “C-pool” value (free of CO₂ readsorption effects) estimated via the titration of active reaction intermediates experiment. We have recently performed similar measurements of the actual “C-pool” (free of CO₂ readsorption effects) on other supported Pt catalysts [5]. As an example, we would like to refer to the case of 0.5 wt% Pt/Ce_{0.8}Ti_{0.2}O_{2-δ} catalyst, where the SSITKA experiment provided a “C-pool” of θ=33.0, whereas the “titration of active reaction intermediates” experiment provided a value of θ=6.5 (actual “C-pool”).

We would like to believe that on the basis of the above clarifications, the readership of this Journal and the scientists who work in the field of SSITKA technique must appreciate our effort to provide for the first time a reliable methodology that allows correcting the “C-pool” measured directly from the SSITKA-Mass spectrometry experiment for the *inherent* external (within the catalytic bed) and internal (within catalyst particle's pore system) CO₂ readsorption effects obtained during WGS.

3. Size of the H-pool

We have read with great caution and interest the comments of the author regarding overestimation of the “H-pool”. Unfortunately, all the views of the author on this issue were not supported by any experimental evidence towards a *quantitative comparison* between the transient rates of H/D exchange via various side reactions leading to the HD(g) production, and the transient rate of

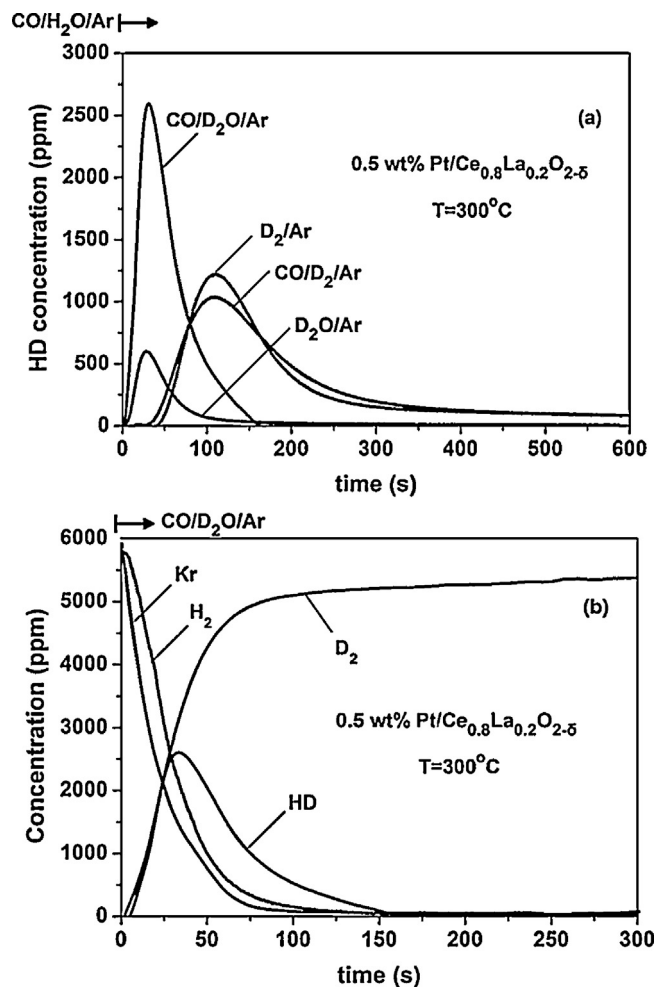


Fig. 1. (a) Transient response curves of HD formation obtained during the following gas switches: 3 vol% CO/10 vol% H₂O/Ar/Kr (2 h, 300 °C) → 3 vol% CO/10 vol% D₂O/Ar (t) (SSITKA switch) or 0.25 vol% D₂/Ar (t) or 3 vol% CO/0.25 vol% D₂/Ar (t) or 10 vol% D₂O/Ar (t); (b) 3 vol% CO/10 vol% H₂O/Ar/Kr (2 h, 300 °C) → 3 vol% CO/10 vol% D₂O/Ar (t) (SSITKA switch to follow the H-path of WGS); W_{cat} = 0.05 g (dilution with SiC, 9:1); F_T = 100 NmL/min.

HD(g) obtained via the WGS during the SSITKA-Mass spectrometry experiment (Fig. 2, ref. [1]). In this Letter to the Editor, we present new advanced transient isotopic experiments, for the first time to our knowledge, which address the issue at hand. It should be pointed out that only H/D exchange relevant to the time-scale and concentrations of involved species during the SSITKA experiment must be considered. This is an important conceptual remark that needs to be noted.

Fig. 1a reports the transient response curves of HD(g) formation obtained during the following gas switches:

- (i) 3 vol% CO/10 vol% H₂O/Ar/Kr (2 h, 300 °C) → 3 vol% CO/10 vol% D₂O/Ar (t) (SSITKA switch)
- (ii) 3 vol% CO/10 vol% H₂O/Ar/Kr (2 h, 300 °C) → 0.25 vol% D₂/Ar (t)
- (iii) 3 vol% CO/10 vol% H₂O/Ar/Kr (2 h, 300 °C) → 3 vol% CO/0.25 vol% D₂/Ar (t)
- (iv) 3 vol% CO/10 vol% H₂O/Ar/Kr (2 h, 300 °C) → 10 vol% D₂O/Ar (t).

For the ease of discussion of the results shown in Fig. 1a, the SSITKA experiment performed to follow the H-path of the WGS is presented in Fig. 1b, and the reasoning behind the design of experiments (ii)–(iv) is explained in what follows.

- The gas switch (ii) probes the kinetics of H/D exchange between the non active “H-containing” species formed under steady-state WGS, the $\text{H}_2\text{O}(\text{g})$ and $\text{H}_2(\text{g})$ gaseous products, which remain in the reactor during the 150 s period of the transient after the switch (see Kr response curve, Fig. 1b), with the produced $\text{D}_2(\text{g})$ during the SSITKA switch (see Fig. 1b). The chosen 0.25 vol% D_2 composition represents the concentration of D_2 produced during the SSITKA switch at the time where the maximum concentration in the HD was formed (see Fig. 1b).
- The gas switch (iii) probes the kinetics of H/D exchange between $\text{D}_2(\text{g})$ and the species mentioned in (a) but in the presence also of 3 vol% CO. This composition of CO simulates the SSITKA conditions (see Fig. 1b), and allows to study the effect of $\text{CO}(\text{g})$ in the H/D exchange processes after comparing the obtained result with that of gas switch (ii).
- The gas switch (iv) probes both the kinetics of H/D exchange between $\text{D}_2\text{O}(\text{g})$ and the species mentioned in (a), and the reaction of $\text{D}_2\text{O}(\text{g})$ with all active “C-containing” species formed under the steady-state WGS reaction. The latter is equivalent to the titration experiment mentioned in Section 2 ($\text{CO}/\text{H}_2\text{O}/\text{Ar} \rightarrow 10 \text{ vol}\% \text{H}_2\text{O}/\text{Ar}$).

The first important observation to be made, based on the results of Fig. 1, is that the HD(g) transient formation rate via H/D exchange processes observed during the D_2/Ar and $\text{CO}/\text{D}_2/\text{Ar}$ gas treatments is largely different from that observed during the SSITKA and $\text{D}_2\text{O}/\text{Ar}$ gas treatments. In particular, there is a significant delay and a large shift towards higher times in the appearance of peak maximum in the rate of HD formation during the D_2/Ar and $\text{CO}/\text{D}_2/\text{Ar}$ gas treatments compared to those of $\text{CO}/\text{D}_2\text{O}/\text{Ar}$ and $\text{D}_2\text{O}/\text{Ar}$. Secondly, at a time of $t = 100$ s after the SSITKA switch, the formation rate of HD(g) is significantly lower than the maximum HD(g) formation rate obtained during the gas switches (ii) and (iii). Third, at a time of $t = 162$ s, where the HD response observed during SSITKA is complete (Fig. 1b), significant HD formation is seen under the D_2/Ar and $\text{CO}/\text{D}_2/\text{Ar}$ gas treatments. These three observations strongly suggest that the rate of HD formation obtained during the SSITKA, and which is controlled by the rate-limiting step present in the H-path towards H_2 formation, must be considered *significantly larger* than the rate of any H/D possible exchange process among the $\text{H}_2(\text{g})$, $\text{H}_2\text{O}(\text{g})$, $\text{D}_2(\text{g})$ and the non active “H-containing” adsorbed species formed during WGS. A *lower limit* for the active “H-pool” can then be defined after subtracting the equivalent amount of H in the HD response of SSITKA from that obtained under the $\text{CO}/\text{D}_2/\text{Ar}$ response up to the time of 162 s (end of the SSITKA-HD transient response curve). The former quantity was estimated to be $282 \mu\text{mol g}^{-1}$ and the latter one $124 \mu\text{mol g}^{-1}$. Thus, the *net amount* of HD(g) corresponds to $158 \mu\text{mol g}^{-1}$, or to an equivalent amount of $\theta_{\text{H}} = 6.07$, expressed in surface monolayers of Pt_s.

The last point to be considered and discussed is the observed HD response under the 10 vol% $\text{D}_2\text{O}/\text{Ar}$ gas treatment (gas switch (iv)). This HD response shows exactly the same peak maximum position in time and very similar shape to that observed during the SSITKA switch (see Fig. 1a). The difference in the absolute concentration values of HD produced among the two gas switches is due to the fact that a larger transient of $\text{D}_2(\text{g})$ (not reported here) than of HD(g) was observed during the $\text{D}_2\text{O}/\text{Ar}$ gas treatment. It is also important to mention here that after the gas switch 10 vol% $\text{H}_2\text{O}/\text{Ar}$ (2 h, 300 °C) \rightarrow 10 vol% $\text{D}_2\text{O}/\text{Ar}$ (t) was applied neither HD nor D_2 gas was observed as previously reported [1]. This result along with the HD responses shown in Fig. 1a for the gas switches (i)–(iv) suggest that adsorbed –OH groups seem not to be able to provide an H/D exchange with the $\text{D}_2\text{O}(\text{g})$ under the applied gas environment relevant to the D_2O -SSITKA switch. On the contrary, upon the switch 10 vol% $\text{H}_2\text{O}/\text{Ar}$ (2 h, 300 °C) \rightarrow 0.5 vol% D_2/Ar (t), a significant production of HD was observed [5] with

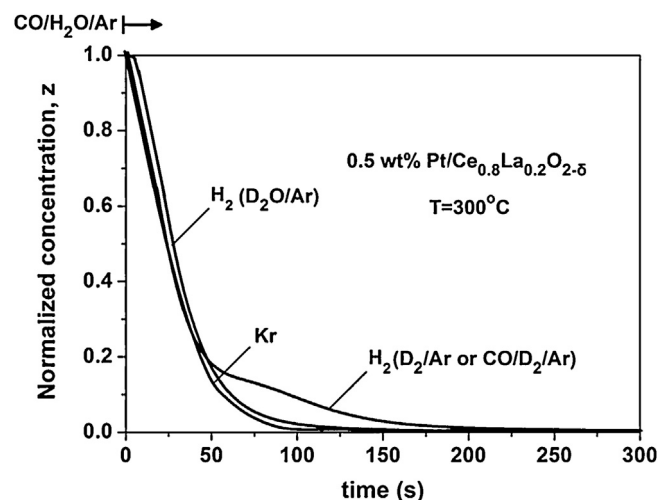


Fig. 2. Transient response curves of the dimensionless gas concentration of H_2 (Z_{H_2}) formed upon the switch 3 vol% $\text{CO}/10 \text{ vol}\% \text{H}_2\text{O}/\text{Ar}/\text{Kr}$ (2 h, 300 °C) \rightarrow 0.25 vol% D_2/Ar (t) or 3 vol% $\text{CO}/0.25 \text{ vol}\% \text{D}_2/\text{Ar}$ (t) or 10 vol% $\text{D}_2\text{O}/\text{Ar}$ (t); $W_{\text{cat}} = 0.05 \text{ g}$ (dilution with SiC , 9:1); $F_T = 100 \text{ NmL/min}$.

a peak maximum formation rate at the same position in time as that observed with the presently used 0.25 vol% D_2/Ar and 3 vol% $\text{CO}/0.25 \text{ vol}\% \text{D}_2/\text{Ar}$ gas treatments (Fig. 1a). These results suggest that –OH groups are able to exchange with $\text{D}_2(\text{g})$ in the presence or absence of $\text{CO}(\text{g})$ to form HD but with *lower rates* when compared to the rate of HD formation via the WGS reaction (SSITKA switch).

Fig. 2 presents the normalized concentration of Kr (tracer) and $\text{H}_2(\text{g})$ formed during the gas switches (ii)–(iv). The Z_{H_2} response observed for the gas switch (iii) was the same as that of gas switch (ii). It is seen that within the first 45 s of the transient, no $\text{H}_2(\text{g})$ is formed in the case of D_2/Ar gas treatment, in harmony with the HD response (Fig. 1a), where the opposite was found for the $\text{D}_2\text{O}/\text{Ar}$ gas treatment. It should be also noted the different Z_{H_2} response observed in the period of 50–250 s during the D_2/Ar and $\text{D}_2\text{O}/\text{Ar}$ gas treatments.

The equivalent amount of H in terms of θ_{H} up to the end of the transient (Fig. 2, 250 s) was found to be 3.5, 3.15 and 1.95 for the D_2/Ar , $\text{CO}/\text{D}_2/\text{Ar}$ and $\text{D}_2\text{O}/\text{Ar}$ gas treatments, respectively. In the case of SSITKA (Fig. 1b), this was found to be $\theta_{\text{H}} = 4.8$. After considering the largest quantity of H/D exchange observed (Fig. 2), and subtracting this from the SSITKA value, a net amount of $\theta_{\text{H}} = 1.3$ is obtained. Thus, the *lower limit* for the active “H-pool” becomes about $\theta_{\text{H}} = 7.4$ (based on the HD and H_2 formed). It is important to point out here that the size of the active “C-pool” provided in Section 2 is $\theta_{\text{C}} = 2.1$. It is very reasonable to argue that θ_{CO} is less than one monolayer (CO-s on Pt), therefore, the amount of the rest “C-containing” intermediate species must be larger than one monolayer. Whether the chemical structure of this is formate (HCOO), or carboxyl (COOH) or both, and since these species contain one H atom per molecular structure, the equivalent “H-pool” must be *larger than one monolayer*. It is also quite unreasonable to support the view that the surface coverage of active H on Pt, and that of –OH groups on both the Pt and the support are zero. We have illustrated in our recent publication [5] that sizes of the “H-pool” in the order of 2–10 surface Pt monolayers correspond to a *reactive zone* length, Δx , formed around each Pt nanoparticle, of less than 30 Å, which means about eight lattice constants of support. For the size of an “H-pool” of $\theta_{\text{H}} = 7.4$, we estimate a reactive zone length of about 22 Å around each Pt nanoparticle of 1.0 nm mean size, thus about *six lattice constants* of $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_2$ support (solid solution). This means that –OH groups are able to diffuse within this zone towards the Pt-support interface, and react with CO on Pt sites

at this interface, to form HCOO and/or COOH *active* intermediate species at 300 °C under WGS reaction conditions; we do not exclude the possibility that surface diffusion of CO towards the Pt-support interface and within this reactive zone to reach the –OH sites to be an energetically favourable step.

On the basis of the results of Figs. 1 and 2, and the discussion previously offered, we believe that we have demonstrated that a careful design of non steady-state transient isotopic and steady-state isotopic transient kinetic analysis (SSITKA) experiments can provide at least a meaningful *lower limit* for the *active* “H-pool” formed in the steady-state WGS reaction over supported metal catalysts. This lower limit of the active “H-pool” becomes very important in order to conclude about the *bifunctional* character of the catalytic WGS at hand. Having estimated a lower limit for the *active* “H-pool” larger than one monolayer (based on the Pt metal surface area), this means that a *reactive zone* located around each Pt metal nanoparticle accommodates part of this *active* “H-pool”. We have demonstrated this result to be the case for the 0.5 wt% Pt/Ce_{1-x}La_xO₂ [1], 0.5 wt% Pt/Ce_{1-x}Ti_xO₂ [4,5] and 0.5 wt% Pt/Ce_{1-x}Zr_xO₂ [11,12] catalytic systems, and we have strengthened this result in the present Letter to the Editor.

4. C-pool/H-pool and main reaction pathway

The author has offered a discussion of a number of very important mechanistic points related to the surface coverage of active reaction intermediates and their relevance to the overall reaction pathway and rate of WGS. In order for the reader to understand correctly the author's discussion and our personal view on this issue, we would first like to note the following. Assuming that the WGS follows only one type of mechanism, e.g. “associative formate or carboxyl with –OH group regeneration”, and the carbon-path from the CO reactant towards the CO₂ gas product can be considered as a *series of pools* of active “C-containing” intermediates (we do not examine here the chemical structure of these intermediates and any CO₂ readsorption effects), then clearly the SSITKA experiment with mass spectrometry (SSITKA-MS) will provide the sum (total) of all these “C-containing” intermediates [13,14]. In this carbon-path, the rate of each elementary reaction step associated with each of these “C-containing” intermediates must be the same. However, this does not imply that the intrinsic reactivity (*k*) of each “C-containing” intermediate is the same or similar. Depending on the magnitude of *k*, the surface coverage of each intermediate is adjusted by the rate-limiting step so as to yield a product *k*. θ = TOF (in a simplified manner). This kinetic concept applies in the SSITKA experiment, where a very large or a very small size of pool of “C-containing” intermediates can be measured. Certainly, if the reactivity (*k*) of an individual “C-containing” intermediate is very large, then its surface coverage may not be experimentally measurable. This result, however, cannot lead to the conclusion that the measured “C-pool” relates to *insignificant* reaction intermediates. A significant reaction intermediate in a *sequence of elementary steps* is the one which participates in the rate-controlling step, thus the one with a low reactivity. As an example, the CO dissociation step (large CO coverage) and not that of –CH_x hydrogenation (very small coverage) was considered as the rate-limiting step of methanation reaction on Rh/γ-Al₂O₃ [8–10]. On the other hand, in the case of Ni/γ-Al₂O₃ [15], both the hydrogenation of –CH_x and CO-s dissociation steps were considered as important steps that control the rate of methanation reaction (similar surface coverages).

In the scenario that the WGS follows two reaction pathways, e.g. “associative formate/carboxyl with –OH group regeneration” and “redox”, the comments provided by the author are valid. The design of appropriate *in situ* experiments to decouple the rate of WGS arising from each carbon pathway is the most desirable effort to be

taken. The author has pointed out previous investigations made by him and his colleagues [16–18], where an experimental methodology was developed that showed that the “associative formate with –OH group regeneration” pathway was contributing to less than 15% in the overall WGS reaction rate, thus formate was considered as a non significant reaction intermediate of the WGS. This methodology [16], however, to our opinion, needs reassessment. The kinetics used to simulate the rate of depletion of the H¹²COO-s species (based on the corresponding IR integral band) during the SSITKA switch was of the form: rate = *k* [formate], implying that the rate-limiting step is associated with the formate species only, and at the same time any other sites/intermediates are not important. For example, decomposition of HCOO-s could involve metal sites (e.g. M = Pt, Au) at the interface, thus the rate should be also proportional to the concentration of these M empty sites. Furthermore, estimation of an *apparent* rate constant associated with the rate of the decomposition step of formate to be compared with the corresponding parameter of the *overall* WGS reaction rate might lead to erroneous conclusions. A kinetic analysis based on *intrinsic* (true elementary steps) than *apparent* site reactivity is the only safe way for such comparisons.

In the publication in discussion [1], we have pointed out that since only one rather symmetrical peak of ¹³CO₂ was observed corresponding to a surface coverage of θ = 2.1 (Fig. 8, ref. [1]), then it was reasonable to suggest that both CO-s and one kind of HCOO-s intermediate follow very similar WGS kinetics towards CO₂ and H₂ formation. We have also pointed out that the small ¹²CO₂ response observed must be due to a very small concentration of a second kind of formate and/or carboxyl species that were not able to exchange with ¹³CO(g) (no H¹²COO-s IR band could be detected) but can react with water with a lower rate than the first kind of formate. The possibility that this small ¹²CO₂ response might be also the result of the reaction between ¹²C-s (formed by the Boudouard rxn under the ¹²CO/Ar gas treatment) with water during the switch to 10 vol% H₂O/Ar cannot be excluded. If the latter is correct, then the very large ¹³CO₂ response observed (θ = 2.1) cannot be assigned to a similar ¹³C-s species formed under the ¹³CO/Ar gas treatment, strengthening the assignment of this large ¹³CO₂ response to the reaction of ¹³CO-s and H¹³COO-s species (evidenced by the red shift in the DRIFTS spectra) in the presence of water.

A micro kinetic analysis to simulate the SSITKA transient response curves in order to investigating rival mechanisms, is another powerful tool to decouple *in a quantitative manner* the rate of WGS in the case where both “redox” and “associative formate or carboxyl with –OH group regeneration” pathways are followed. This approach was demonstrated in the case of the more complex Fischer-Tropsch catalytic reaction mechanisms [19].

5. Concluding remarks

On the basis of the clarifications and comments provided in the previous sections, no reassessment is necessary on the following conclusions of the publication in discussion [1]:

- (i) The size of the *active* “C-pool” and “H-pool” formed in the WGS reaction over the 0.5 wt% Pt/Ce_{1-x}La_xO_{2-δ} catalysts is equivalent to *several monolayers of surface Pt*. Therefore, the active species cannot reside only on the Pt surface. Most of them are formed within a region of about 22 Å around each Pt nanoparticle. This result demonstrates the *bifunctional* catalytic role of the present supported Pt catalyst in the WGS reaction. The exact concentration of “C-pool” and “H-pool” cannot be determined from the corresponding ¹³CO-SSITKA and D₂O-SSITKA gas switches due to CO₂ readsorption and H/D side exchange reactions, respectively, that occur

during the transients. However, *novel operando* experimental methodologies using appropriate gas switches following steady-state WGS can provide a good estimate of the active “C-pool” free of CO₂ readsorption effects (both external and internal of catalyst particles). A good estimate of the active “H-pool” via the D₂O-SSITKA experiment is feasible only if the rates of the various H/D exchange processes are *small* compared to the WGS reaction rate leading to hydrogen production *over the transient period of the SSITKA switch*. We have reported here a methodology to account for these H/D exchange processes, where a *lower limit* of the size of the active “H-pool” can be provided.

- (ii) The *chemical nature* of several active species participating in the WGS reaction path(s) was identified correctly by SSITKA-DRIFTS and other non steady-state transient isotopic experiments irrespectively of their major or minor contribution to the overall reaction rate of WGS. It is obvious that reaction intermediates of very high activity cannot be measured experimentally either by DRIFTS or any other technique for catalytic studies at 1 bar total pressure using flow reactors. They can only be identified by theoretical studies [20,21] when proper model catalytic surfaces are used to simulate polycrystalline supported metal catalysts.
- (iii) We have shown that both “redox” and “associative formate/carboxyl with–OH group regeneration” mechanisms operate on the present 0.5 wt% Pt/Ce_{1–x}La_xO_{2–δ} catalysts in the 250–300 °C range, in harmony with recent theoretical DFT studies on Pt/CeO₂ (1 1 1) surfaces [21].

The *extent of contribution of each mechanism* operating in the WGS, and thus the *significance* of the active “carbon-containing” intermediates identified needs to be reassessed according to the comments provided in Section 4.

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